

Application of In-line High Shear Mixing Process in the Oxidative-Adsorptive Desulfurization of Diesel Fuel

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Abstract. The removal of sulfur from diesel fuel has attracted the attention of many researchers due to the more stringent regulations imposed on the allowable sulfur content of diesel in many countries. Environmental regulations in the Philippines have set the allowable sulfur content of diesel to less than 50 ppm by 2016. Oxidation using in-line mixing followed by adsorption is a promising desulfurization technology that can be explored. This paper presents the results of experimental investigations of oxidative desulfurization of diesel fuel using continuous high-shear mixing CSTR and in-line mixing set-ups. Alumina was used for fixed-bed adsorption of oxidized sulfur compounds. The effects oxidation parameters namely reaction temperature, high shear mixing speed, diesel flow rate on sulfur removal were investigated. At 82% sulfur removal, in-line mixing flow rate was 500 ml/ min while CSTR flow rate was 360 ml/ 30 min (12 ml/min). Optimal oxidation operating parameters using Box-Behnken Design were 18000 rpm high shear mixing speed, 500 ml per min of diesel and 300 ml per min of hydrogen peroxide. Increasing the amount of adsorbent alumina from 5 to 15 g decreases the residual sulfur in diesel fuel from 265 to 30 ppm at 70 °C. In this study, the sulfur content of diesel fuel was reduced from 1480.4 ppm to 30 ppm which is well within the limit of 50 ppm for Euro IV standard.

Keywords: box-behnken design, continuous high shear mixer, oxidative desulfurization, UAOD

1. Introduction

Removal of sulfur from diesel has attracted the attention of many researchers due to strict regulations imposed on the sulfur content of fuel in many countries. Environmental regulations have set the sulfur content of diesel to less than 15 ppm in the United States and 50 ppm in other countries [1]. The hydrodesulfurization (HDS) process has been the most commonly used for the past several years to remove sulfur compounds. Hydrodesulfurization can eliminate the refractory sulfur but the process is very expensive and it is performed under very high temperature and pressure conditions [2].

In order to further lower the concentration of sulfur, challenging and new technologies are needed. Alternative desulfurization processes are therefore necessary to produce low sulfur-content diesel. Some of the possible alternatives to HDS are oxidative desulfurization, bio-desulfurization, reactive adsorption, non-destructive adsorption, N-adsorption and extraction [3].

Oxidative desulfurization is considered to be one of the most promising alternatives to HDS. ODS presents several advantages compared with HDS. In ODS, the refractory-substituted dibenzothiophenes (DBTs) are easily oxidized under low temperature and pressure conditions and expensive hydrogen is not necessary. Therefore, the capital requirement for an ODS unit is lower than that for a deep HDS unit [4].

ODS generally involves two steps: (1) sulfur-containing compounds in diesel are oxidized to their corresponding sulfoxides and sulfones by an oxidant and (2) sulfoxides and sulfones are removed from diesel

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by extraction, adsorption or distillation [5]. Currently, a combined process of ultrasound-assisted oxidation and adsorption has demonstrated favorable results in achieving ultra low sulfur diesel (ULSD). The principle behind these techniques involves the conversion of refractory sulfur and other sulfur containing compounds into their corresponding sulfoxides and sulfones using transition catalyst, phase transfer agent and ultrasound power [6], [7]. These more polar products can be easily removed by solid adsorption at low temperature and ambient pressure. The adsorption of the oxidized sulfur compounds such as dibenzothiophene sulfone (DBTO) onto solid adsorbents allows for their removal from fuel without the addition of chemicals [8].

Developing the new chemical reactor involves major technical and financial considerations to meet a definite and practical need of the industries. The nature of continuous flow reactor permits a long production runs of high volume fuel streams in petroleum refining industries. In a continuously stirred tank reactor, the mixing continues until the desired product quality is achieved. A tank and a rotary mixer are needed. In a mixing tank, more interactions happen near the mixing blades and decreases as the distance from the mixer increases. Another type of mixing equipment other than CSTR is the in-line mixer. There are two types of in-line mixers: static and dynamic. A static in-line mixer has no moving parts and no energy required. Baffles are installed to change the flow patterns of liquids. In dynamic in-line mixing, electric motor is used and the mixer performs a rotary motion about the axis of the flow. The mixing equipment is installed in a pipeline. It ensures that the whole mixture will be processed as it flows through the mixing vessel. In-line mixing ensures the consistent flow and uniform mixing of the reactants before oxidation (Bematek, 2005). Therefore, the main objective of this study is to determine the percent removal of sulfur containing compounds in diesel fuel using high shear mixing (the continuously stirred tank reactor (CSTR) and in-line high shear mixing) in oxidative desulfurization and alumina as adsorbent.

2. Materials and Methods

2.1. Chemical and materials

Diesel fuel sample with approximately 1000ppm sulfur was purchased from Taichin Global Co. Aluminum oxide, neutral with 150mesh was obtained from Aldrich Company. Hydrogen peroxide with 50% concentration, tetraoctyl ammonium bromide with 98% purity and phosphotungstic acid with purity of 98% were all purchased from Merck.

2.2. Chemical and materials

A continuous set-up using high shear mixing (the continuously stirred tank reactor (CSTR) and in-line high shear mixing) for oxidative desulfurization of diesel fuel was made, shown as Fig. 1. Oxidized diesel was then subjected to adsorption using alumina as adsorbent. IKA Ultra Turrax T25 digital was used as the high shear mixer. Response surface methodology (RSM) was used in this experiment to determine the most optimized condition for the removal of sulfur in diesel fuel. Box-Behnken Design (BBD) for Response Surface Methodology (RSM) was specifically used to determine the optimum parameters. The mixer speed, diesel flow rate and hydrogen peroxide flow rate were the parameters investigated in this study.



(a) Setup of continuously stirred tank reactor



(b) Setup of in-line high shear mixer

Fig. 1: Oxidation set-up using high shar mixing.

2.3. Analysis using TSA and GC-SCD

Adsorbed diesel was tested for sulfur content using TSA (Total Sulfur Analyzer). Validation of sulfur content was investigated using GC-SCD. Gas Chromatography GC Agilent 7890A with Sulfur Chemiluminescence Detector (GC-SCD) was used to analyze the sulfur containing compounds in diesel fuel qualitatively. The GC-SCD has higher selectivity and sensitivity towards sulfur-containing compounds. In quantifying the concentration of sulfur, it uses linear equation which makes it more favourable.

The column of GC-SCD used was a fused-silica capillary column with 0.25 mm I.D., 30 meters length and 0.25 mm film thickness. The injector temperature was initially set at 280 °C. The column temperature was set at 100 °C for one minute and increases at 20 °C/ min until it reaches a final temperature of 280 °C. The analysis of sulfur content using GC-SCD was done in reference to appropriate standard solution. Sulfur content was determined using the calibration curve for oxidized dibenzothiophene.

3. Results and Discussions

3.1. Oxidation using high shear mixing

The comparison between an in-line mixer and a CSTR in terms of flow rate is shown in Fig. 2. At the same 82% sulfur removal, the in-line mixer flow rate is 500 ml/ min while the CSTR flow rate is 360 ml/ 30 min (12 ml/ min). The effective flow rate in an in-line mixer is much higher compared to CSTR for equivalent sulfur removal. This allows the former to handle significantly larger volumes of diesel fuel compared to latter. In in-line mixing, the entire batch of flow entering the mixer is processed uniformly. In a CSTR, the system needs an extended operating time to process one batch of flow liquids. This is because the mixer in CSTR does not provide uniform mixing throughout the tank.

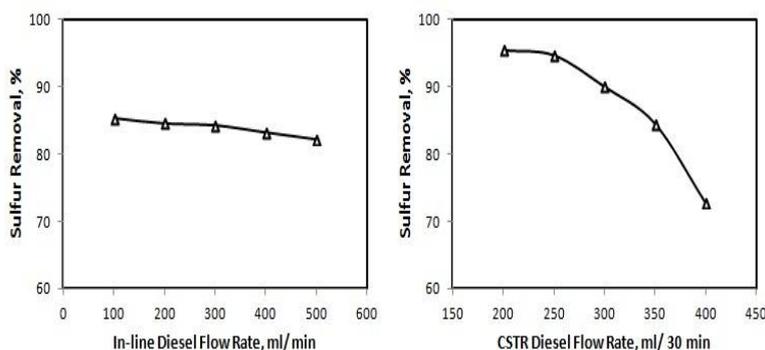


Fig. 2: Comparison of in-line mixer and CSTR.

3.2. Box-Behnken design analysis

Diesel fuel flow rate, hydrogen peroxide flow rate and in-line high shear mixing speed were optimized using Box-Behnken Design. A three-level, three-factor design was used as shown in Table 1. Design Expert 7.0 was used for data analysis and optimization.

Table 1: The control factors of Box-Behnken Design.

Factors	Coded level		
	-	0	+
Mixer speed, rpm	10,000	14,000	18,000
H2O2 flow rate, ml per min	100	300	500
Diesel flow rate, ml per min	100	300	500

Table 2 shows the results from BBD. The highest sulfur removal of 82% was achieved at 18000 rpm, 500 ml/min diesel fuel flow rate and 300 ml/min hydrogen peroxide flow rate. The lowest sulfur removal of 37% was observed at 10000 rpm, 300 ml/ min diesel fuel flow rate and 100 ml/ min hydrogen peroxide flow rate. Moreover, increasing the high shear mixer speed increases the percent sulfur removal even with increasing diesel and hydrogen peroxide flow rate. The ranges of values used in the experiment are 10000, 14000 and 18000 rpm and 100, 300 and 500 ml per minute of flow rate each for diesel and hydrogen

peroxide. The optimum values are 18000 rpm high shear mixer speed, 500ml per minute of diesel flow rate and 300ml per minute of hydrogen peroxide flow rate.

Table 2: Box-Benhken design for the in-line mixing experiments.

Run	Mixer speed, rpm	Diesel flow rate, ml/ min	Hydrogen Peroxide flow rate, ml/ min	Sulfur Removal, %
1	14000	300	300	66.2
2	14000	100	100	63.0
3	14000	300	300	66.5
4	18000	300	500	75.5
5	14000	500	100	60.0
6	10000	500	300	70.0
7	14000	100	500	73.4
8	18000	100	300	82.0
9	10000	100	300	78.8
10	14000	500	500	72.7
11	14000	300	300	73.1
12	10000	300	500	69.4
13	14000	300	300	73.1
14	18000	500	300	82.1
15	10000	300	100	37.4
16	14000	300	300	66.2
17	18000	300	100	72.0

3.3. Effect of increasing amount of alumina

Using the optimum value, the oxidized diesel is subjected to increasing amount of adsorbent alumina. Fig. 3 shows that increasing the amount of alumina used from 5 to 15 g, the residual sulfur compounds in diesel fuel decreased from 265 to 30 ppm (98% removal). The lowest concentration of residual sulfur compounds found on diesel fuel was 30 ppm using 15 g of alumina. This is within the 50 ppm limit of the Euro IV standard.

Chen et al. studied the use of ultrasound and alumina as adsorbent in desulfurization of diesel fuel and pyrolysis oil. Desulfurization of diesel fuel using 15 g of alumina resulted to 186.3 ppm residual sulfur while that using 30 g produced 2.7 ppm residual sulfur [9].

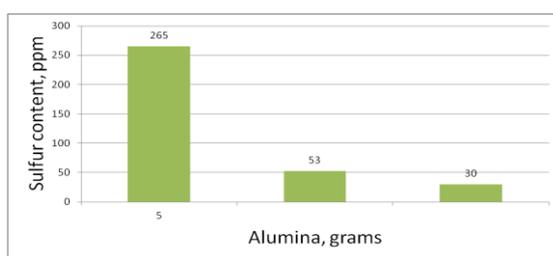


Fig. 3: Residual sulfur at varying amount of alumina (T = 70 °C, diesel flow rate = 500 ml/min, hydrogen peroxide flow rate = 300 ml/ min, mixer speed = 18000 rpm).

3.4. GC-SCD analysis

To validate the results of the Total Sulfur Analyzer on the remaining sulfur compounds on diesel fuel, parallel testing was done using GC-SCD. Figure 4 shows the GC-SCD result which is qualitative in nature. Fig 4a shows the sulfur containing compounds from original diesel fuel sample, Fig 4b shows the oxidized sulfur compounds and Fig 4c shows the desulfurized diesel fuel. Notice the disappearance of peaks indicating the removal of sulfur compounds. Chen et al also uses GC-SCD to monitor the removal of sulfur compounds from diesel fuel after using ultrasound assisted oxidative desulfurization (UAOD) and adsorption. Original diesel sample and desulfurized diesel were compared. No major peaks of sulfur compounds were found after desulfurization [9]. It clearly shows the organic sulfur compounds have been successfully removed from the diesel.

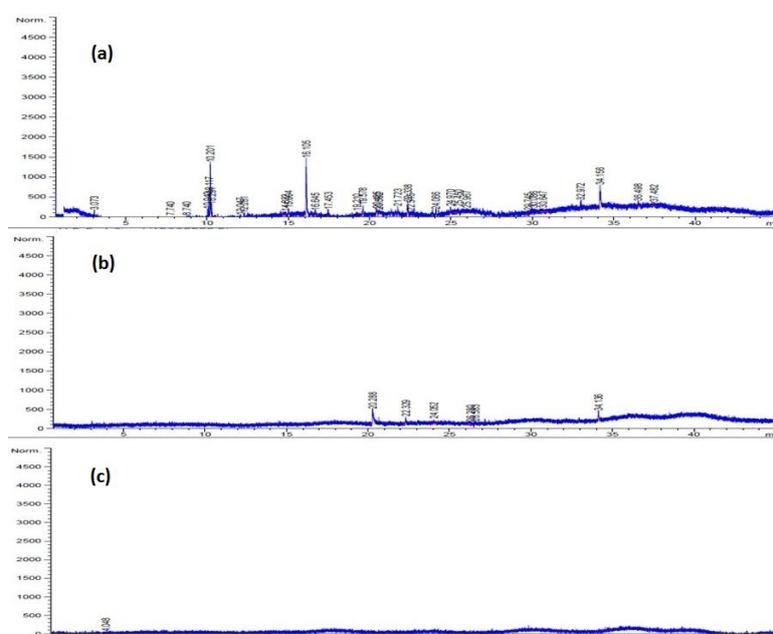


Fig. 4: GC-SCD results of pure diesel sample, oxidized and adsorbed diesel.

4. Conclusion

Desulfurization of diesel fuel using oxidation and adsorption is an effective alternative to hydrodesulfurization method with up to 98% efficiency. Diesel sample with 1480.4 ppm sulfur content can be reduced up to 30 ppm, which is well within the limit of 50 ppm for Euro IV standard. An economical approach using in-line high shear mixing is proven to be suitable for continuous operation with less capital cost. In-line mixers can be easily installed on existing pipelines.

5. Acknowledgements

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6. References

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